Discussion Section Exercise Solutions:
EI Fragmentation

1. I think one way to approach this problem as a whole was to think about what radical cations might be generated by EI on cocaine, and what fragments might be generated from those cations. There are three lone pairs that are likely sites of ionization:

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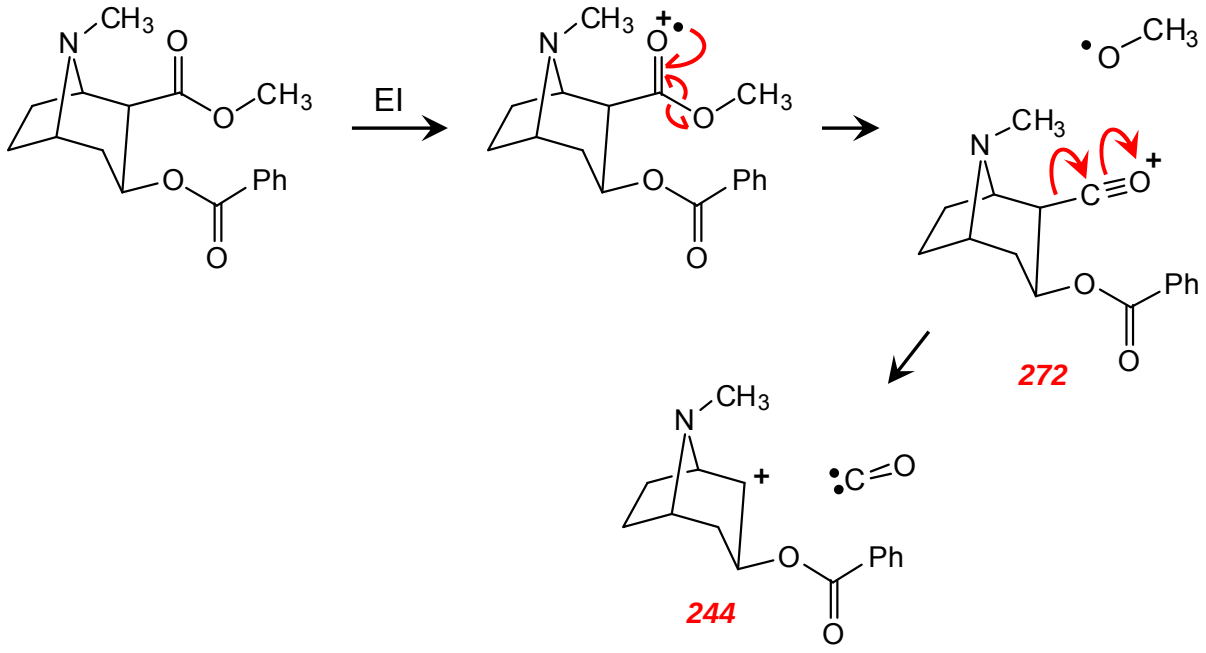
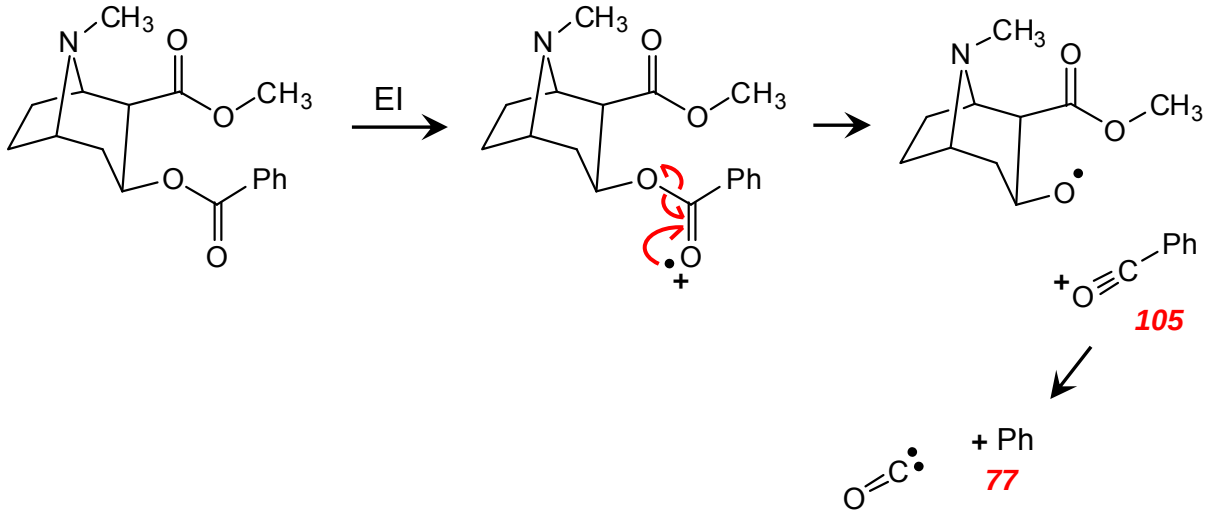
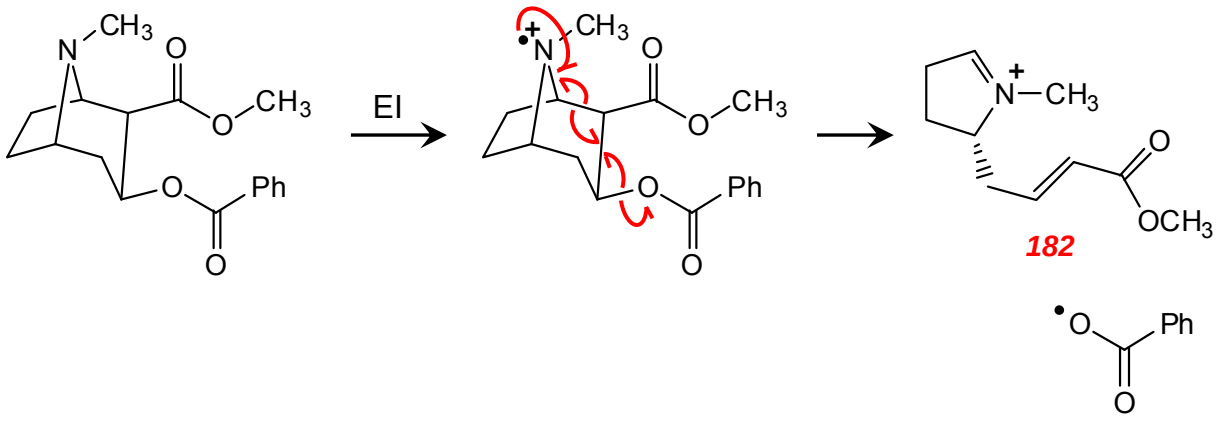


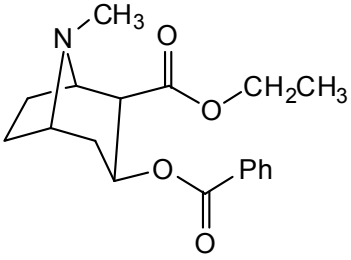




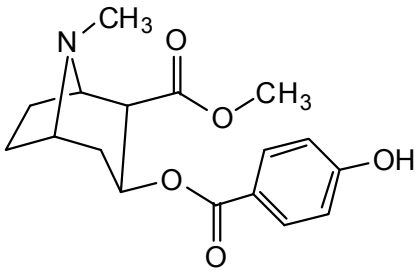
a. The above fragmentation patterns actually describe all of the higher-mass fragments except the peak at *m* = 198, which would be a loss of Ph-C=O radical. It's not clear how this would be lost.

b. 105 and 77 are pretty simple to explain. All of the others require multiple bond cleavages in the bicyclic ring structure.

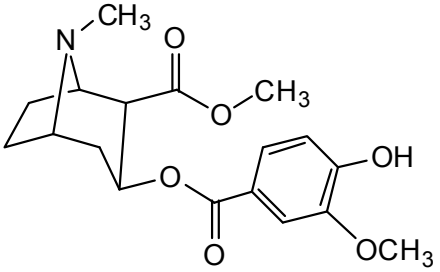
c. <u>Top spectrum:</u> The parent mass is 14 amu higher (a -CH_2- group?). The spectrum has the same *m*/*z* = 272 fragment peak as cocaine does, which suggests that the extra mass must be in R_1. An easy explanation for this would be that it is the ethyl ester instead of the methyl ester.



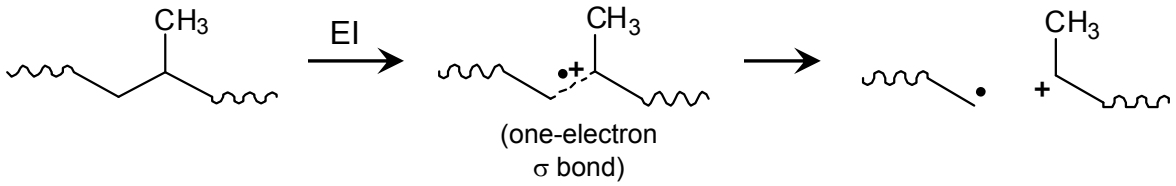
<u>Middle spectrum:</u> This parent is 16 amu higher than cocaine (an oxygen atom?). The loss of •OCH_3 (319 → 288) happens just as it does in cocaine, so the extra mass must be in R_2. The phenyl group could certainly have an oxygen in it:



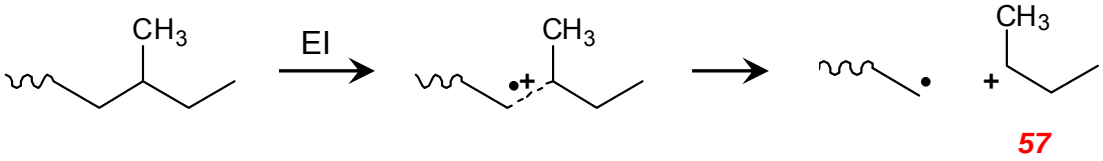
<u>Bottom spectrum:</u> Parent is 46 amu higher. Loss of •OR_1 is 31 (349 → 318), which again is likely •OCH_3, and all 46 mass units must be in R_2. (Also matches the fact that 105 peak has moved to 151.) Could be two oxygens and a CH_2:



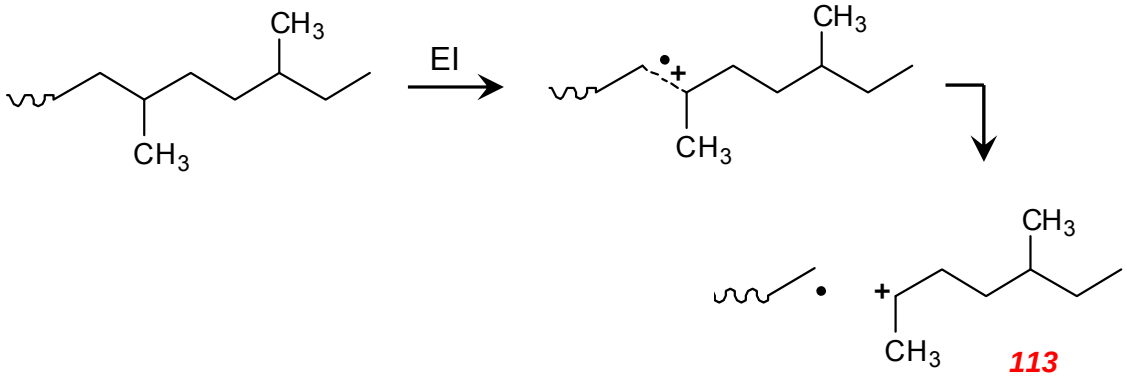
2. Our alkane is going to ionize and cleave preferentially at the most substituted junctions. In addition, the more substituted fragment will carry the charge over the less substituted fragment, which will inherit the radical.



So, the most prominent fragment peaks in the mass spectrum—the peaks at *m*/*z* = 57, 113, and 183—should correspond to this type of fragmentation. Using the mass 57 fragment as the easiest illustration,



So one methyl is three carbons in from the end. Where is the other one?



The *m*/*z* = 183 fragment comes from breaking the alkane on the other side of this same methyl group. So the overall alkane structure is